

# Gallium-Palladium Alloys As Dental Filling Material

RICHARD M. WATERSTRAT  
ROBERT W. LONGTON



The remarkable ability of liquid gallium to "wet" the surfaces of many solids, including human teeth (1), has stimulated interest in gallium alloys as possible filling materials in dentistry (1, 2). A number of gallium alloys which possess some of the properties necessary in dental filling materials have been reported (1-4). Several have also been described by C. W. Austin, Jr., at the National Bureau of Standards, and J. P. Lyle, of the Aluminum Corporation of America. Most of these alloys were subsequently found to lack other necessary properties such as strength, corrosion resistance, or tolerance by biological tissues. A more inert alloying ingredient is apparently needed to make the gallium alloys nonreactive in the oral environment. Such requirements lead to a consideration of the "noble" metals, such as gold and the metals of the platinum group in the periodic table, as possible alloy ingredients. Since palladium is the least expensive of the noble metals, it was selected for further investigation as a constituent of gallium alloys.

## *Preparation of Alloys*

The gallium alloys were prepared in a manner familiar to many users of dental amalgam, that is, by trituration of the liquid gallium with the solid metal powder in a ground glass mortar and pestle. The plastic mixture was then packed into a suitable mold from which it was

---

*Mr. Waterstrat is a research associate of the American Dental Association at the National Bureau of Standards, Washington, D.C. Commander R. W. Longton, U.S. Navy Dental Corps, obtained the data on particle size effects in the gallium-palladium alloys while he was a guest worker at the National Bureau of Standards.*

subsequently removed and allowed to harden in air.

In most cases a gallium solution (eutectic) containing 11 percent tin was used since tin lowers the melting point of gallium from slightly above room temperature to about 20° C. and thus permits the retention of gallium in the liquid state at room temperature for greater convenience in mixing the alloy.

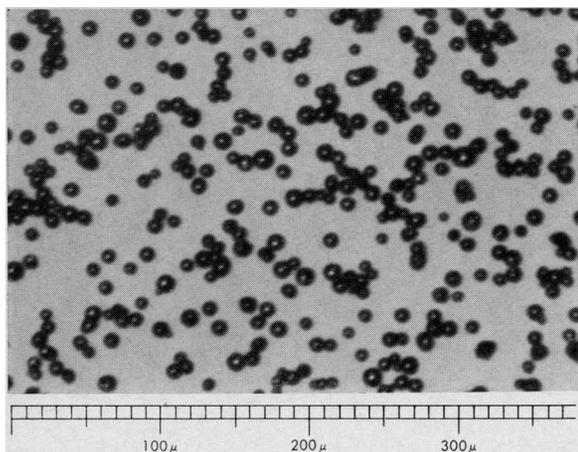
The alloys were allowed to harden for at least 24 hours before subjecting them to the various tests.

## *Variation of Particle Size*

It was recognized at the beginning of this investigation that the particle size of the metal powders would probably have a pronounced effect on the properties of the hardened gallium alloys. A recent investigation (5) has shown that the mechanical properties of dental amalgam are greatly influenced by alloy particle size. The specimens used in the investigation were prepared using spherical alloy particles in graded size increments. In our study (6) spherical metal powders were also used for the gallium-palladium alloys. These spherical powders of pure palladium (A) prepared by a patented process, were separated into various size increments by sieving and elutriation. A typical photomicrograph of the spherical powder is shown in figure 1. The size ranges into which the spherical particles were separated and the percentage yield in each particle size range are given in table 1. Only insignificant quantities of spherical powder are obtained in sizes below 4 microns. In order to investigate the effect of using smaller particle sizes, it was necessary to obtain a commercial grade of fine palladium powder in which the particles were not spherical but irregular in shape. These powders, however, were less than 1 micron in size. In some cases they were mixed with larger particle size ranges of the spherical powders to produce a composite of large and small particles.

## *Exothermic Reaction*

When using the fine powder it was necessary to take certain precautions during mixing in order to avoid a violent exothermic reaction between the palladium and the liquid gallium-



**Figure 1. Photomicrograph of a spherical palladium powder**

tin solution. The heat evolved during this reaction was sufficient to cause the mixture to become red hot and to melt the alloy. This reaction was not observed with any of the spherical alloy powders. It could also be suppressed through a slight cooling of the mortar and pestle and of the alloy ingredients by placing them in a refrigerator before mixing. The reaction could be prevented by mixing the fine powder with an excess of two or three times its weight of liquid gallium solution and subsequently expressing this excess after completion of the mixing. The resulting "dry" mix, however, might still ignite unless it was immediately cut into pieces about one-fourth inch in diameter before being packed into the steel molds. In no instance was any temperature rise noted after packing in the molds or during hardening. The relatively cool surfaces in contact with the alloy evidently conduct heat away from the alloy mixture at a rate sufficient to prevent a temperature rise in the packed specimens. The pure palladium could be replaced by a palladium solid solution, and thus the amount of heat evolved would be reduced through a simple dilution effect. A relatively small dilution suffices to subdue the exothermic reaction, as will be noted in a subsequent description.

### *Identifying Alloy Constituents*

During the course of this investigation, the binary gallium-palladium phase diagram published by Shubert and associates (7) was of

great help in identifying the alloy constituents. The major product of the hardening reaction was identified as intermediate phase PdGa<sub>5</sub>, which is the binary intermediate phase containing the highest percentage of gallium. X-ray diffraction patterns in all cases showed significant traces of unreacted palladium in the hardened alloy specimens. The specimens which had been melted by exothermic heating were also examined by X-ray diffraction and were found to consist of intermediate phase PdGa with no evidence of any residual palladium or of any other phase. This indicates that the overall composition of the gallium-palladium alloys is approximately 50 percent each of gallium and palladium. The hardening reaction occurring at room temperature, therefore, does not represent an equilibrium situation since the PdGa<sub>5</sub> phase and unreacted palladium could presumably undergo further reaction to form the phase PdGa. Although the phase diagram indicates that other binary phases might be expected to form at room tem-

**Table 1. Size ranges of spherical palladium powders and percent distribution in each size range**

Size	Method	U.S. sieve numbers and flow rates	Particle diameter (microns)	Percent palladium of total <sup>1</sup>
11-----	Sieving-----	R-50 <sup>2</sup>	297	6.7
10-----	Sieving-----	P-50 R-70	210-297	10.6
9-----	Sieving-----	P-70 R-100	149-210	10.8
8-----	Sieving-----	P-100 R-140	105-149	22.9
7-----	Sieving-----	P-140 R-200	74-105	17.0
6-----	{ Sieving Elutriation	P-200 R-11.00 <sup>3</sup>	50-74	18.2
5-----	Elutriation	P-11.00 R-5.08	30-50	5.1
4-----	Elutriation	P-5.08 R-2.00	15-30	4.3
3-----	Elutriation	P-2.00 R-1.02	8-15	1.3
2-----	Elutriation	P-1.02 R-0.68	4-8	.6
1-----	Elutriation	P-0.68	0-4	-----

<sup>1</sup> Lost 2.4 percent of total.

<sup>2</sup> Mesh number of U.S. Standard sieve.

<sup>3</sup> Flow rate, ml./sec.

NOTE: R=Retained on the numbered sieve or remained in the column or flask.  
P=Passed through the numbered sieve or flowed into the collecting tube.

perature, only the PdGa<sub>5</sub> phase and palladium were detected in the X-ray patterns.

The most stable intermediate phase in the binary gallium-palladium system is the one designated as Pd<sub>2</sub>Ga. Since dilution of pure palladium was desirable in order to control the exothermic reaction mentioned previously, it was felt that perhaps by mixing Pd<sub>2</sub>Ga rather than pure palladium with the gallium solution, the amount of heat evolved would be significantly reduced. This appeared to be the case, since finely powdered Pd<sub>2</sub>Ga reacted at room temperature to produce a very strong alloy with no detectable temperature rise. Thus the dilution of pure palladium with 33 atom-percent gallium appears to be more than adequate to control the exothermic reaction. The products of the hardening reaction between Pd<sub>2</sub>Ga and the gallium solution were identified as PdGa<sub>5</sub> plus a small amount of unreacted Pd<sub>2</sub>Ga.

#### Mechanical Properties

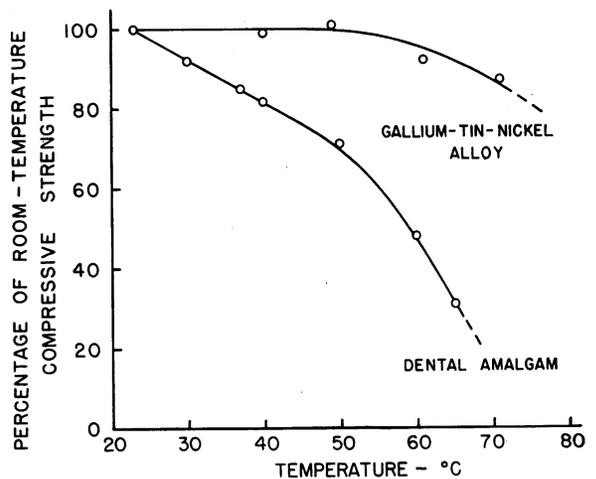
As had been expected, the mechanical properties of gallium-palladium alloys were found to depend greatly on the particle size of the palladium powders used in preparing the alloys. In general, the smaller particle sizes produced alloys which were stronger and showed less expansion during hardening than the alloys prepared from coarser sizes. Typical test values for a gallium-palladium alloy are given in table 2 together with values obtained for a good commercial dental amalgam tested under the same conditions.

The tests for compressive strength, shear strength, and tensile strength are quite helpful in evaluating the performance of gallium alloys

**Table 2. Properties of gallium-palladium alloy compared with dental amalgam**

Alloy properties	Dental amalgam	Gallium-tin-palladium
Compressive strength (24 hours).	45,000 psi...	61,000 psi.
Shear strength (24 hours).	18,000 psi...	21,000 psi.
Tensile strength (5 weeks).	8,000 psi....	8,000 psi.
Setting change (5 days)...	0.1 percent..	1.0 percent.
Approximate final setting time.	3 hours.....	5 hours.
Coefficient of thermal expansion.	25×10 <sup>-6</sup> /°C.	17×10 <sup>-6</sup> /°C.
Approximate density.....	12 gm./cc....	8 gm./cc.

**Figure 2. Temperature dependence of compressive strength**



compared with dental amalgam. However, it is by the use of rheological creep tests involving measurements of strain versus time, under a constant tensile stress, that the most significant differences in behavior are revealed. These NBS tests, performed by Oglesby and Waterstrat, were made at room temperature and at stresses corresponding to approximately one-half the ultimate tensile strength. The results of these tests indicated that, compared with dental amalgam, the gallium-palladium alloys exhibit a nearly negligible amount of flow (creep), whereas dental amalgams under the same conditions flow to such an extent that fracture may occur. The clinical significance of these properties is not yet known, but recent NBS research, reported by G. F. Petersen, suggested that the flow of amalgam under load, plus the effects of differential thermal expansion between the amalgam and the tooth, may produce the marginal defects known as ditching that are often observed in clinical fillings. It appears that the filling is slightly raised above the surface of the tooth, and the edges are subsequently broken off to produce a "ditch" at the margin of the restoration. This might be prevented through the use of gallium-palladium alloys because of their high strength and resistance to flow as well as their smaller differential thermal expansion with respect to the tooth.

Figure 2 shows the relationship between compressive strength and temperature for dental amalgam and a gallium-nickel alloy. Although

dental amalgam loses a large percentage of its strength at the elevated temperatures (37° C.-60° C.) frequently encountered in the mouth, the gallium alloys retain nearly full strength throughout this temperature range. Their higher melting temperatures are believed to be at least partly responsible for this effect.

#### *Coefficient of Thermal Expansion*

Comparison of the thermal expansion coefficients for dental amalgam, gallium-palladium alloys and human teeth reveals that a significantly smaller differential thermal expansion would exist between teeth and the gallium-palladium alloys than between teeth and dental amalgam (fig. 3). This smaller differential thermal expansion may help to prevent marginal leakage between the filling and the tooth.

#### *Biological and Corrosion Studies*

A carcinogenic reaction has been reported from subdermal implants of gallium-nickel alloys in rats (8). A similar study of subdermal implants of gallium-palladium alloys in rats for up to 1 year has not produced tumors (9), but tissue reactions were observed to be more severe than with similar implants of dental amalgam. A migration of alloy fragments of the implant into the surrounding tissues was observed with bizarre cell reaction, necrosis, and purulent exudate. These observations involving subdermal implants are being supplemented by studies of gallium-palladium fillings in human vital teeth. Preliminary results for

dogs indicate no pulp irritation or blackening of the teeth by the gallium-palladium alloys (9).

Studies of corrosion are also in progress. A blackening of the gallium-palladium fillings in dogs apparently occurs under certain conditions although polished samples may be immersed in human saliva at mouth temperature for several months with no observable change in color. Considerable changes in alloy composition are possible which could markedly improve their corrosion resistance.

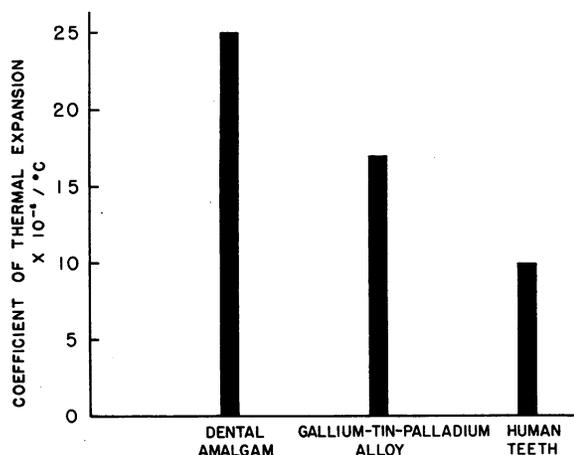
#### *Discussion*

The study of gallium-palladium alloys has shown that they offer considerable promise as dental filling materials. Long-term studies of their corrosion resistance and tissue tolerance are now underway. Mechanical properties can be suitably controlled by using metal powders in graded size increments. Exothermic reactions can be controlled by using the optimum particle size ranges as well as through alloy additions.

The setting expansion listed in table 2 is a sensitive function of particle size. American Dental Association Specification No. 1 for Alloy for Dental Amalgam (10) sets an upper limit of 20  $\mu$ /cm. for setting expansion, but this figure applies only to the dental amalgam alloys. It was set at a reasonable upper limit which is readily achieved in the use of dental amalgams. There is some clinical evidence to suggest that excessive contraction during hardening is undesirable, but there is not enough clinical evidence at present to establish the upper limit for the setting expansion of a dental filling. The setting expansion can be significantly reduced through the use of smaller particle sizes if clinical data indicate that a smaller expansion is desirable. Longer setting times are generally required for the gallium-palladium alloys, but this is also a sensitive function of particle size and can be improved. The setting times given in table 2 are for comparative purposes only and were derived from data on setting expansion versus time.

The use of other noble metals alloyed with the palladium may exert a considerable influence on the properties of the gallium-palladium alloys. We have produced experimental specimens of hardenable gallium alloys by using pure

**Figure 3. Thermal expansion coefficients**



gold, pure platinum, pure iridium, and pure rhodium in combination with the gallium solution. All these alloys harden at room or mouth temperature and possess a wide range of properties. By suitable alloying of these elements with each other or with pure palladium, a considerable variation in properties can be obtained for their respective gallium alloys.

The use of intermediate phases containing high percentages of palladium such as Pd<sub>2</sub>Ga can also produce hard gallium alloys, and intermediate phases of the other platinum-group metals might also be used.

### Summary and Conclusions

As a result of this research it has been established that gallium-palladium alloys possess a number of properties which may make them superior to dental amalgam as a restorative dental material.

1. An ability to "wet" the tooth structure.
2. Higher strengths and greater resistance to flow.
3. Greater retention of strength at higher temperatures.
4. A thermal expansion coefficient closer to that of human teeth.

At present the only obvious obstacle to the use of gallium-palladium alloys in dental fillings is inadequate knowledge of their tissue tolerance and of their stability in the oral environment. A considerable latitude exists for alloying palladium with other noble metals in order to improve the properties of the gallium-palladium alloys.

### SUPPLY REFERENCE

- (A) Palladium powders supplied by Federal Mogul Division, Federal-Mogul-Bower Bearings, Inc., Ann Arbor, Mich.

### REFERENCES

- (1) Smith, D. L., and Caul, H. J.: Alloys of gallium with powdered metals as possible replacement for dental amalgams. *J Amer Dent Assoc* 53: 315 (1956).
- (2) Smith, D. L., Caul, H. J., and Sweeney, W. T.: Some physical properties of gallium-copper-tin alloys. *J Amer Dent Assoc* 53: 677 (1956).
- (3) Lyle, J. P.: U.S. Patent 2,585,393.
- (4) Smith, D. L., and Caul, H. J.: U.S. Patent 2,864,695.

- (5) Demaree, N. C., and Taylor, D. F.: Properties of dental amalgams made from spherical alloy particles. *J Dent Res* 41: 890 (1962).
- (6) Longton, R. W.: Properties of dental amalgams and gallium alloys produced by using spherical alloy powders. Thesis. Georgetown University, Washington, D.C., 1963.
- (7) Shubert, K., Lukas, H. L., Meisner, H. G., and Bhan, S.: The diagrams of the systems cobalt-gallium, palladium-gallium, palladium-tin and related alloys. *Z Metallkunde* 50: 534 (1959).
- (8) Mitchell, D. F., Shankwalker, G. B., and Shazer, S.: Determining the tumorigenicity of dental materials. *J Dent Res* 39: 1023 (1960).
- (9) Longton, R. W., Ostrom, C. A., Lyon, H. W., and Miller, C. R.: Results of a preliminary pilot study. Dental Division, Naval Medical Research Institute, Washington, D.C., 1963.
- (10) American Dental Association: American Dental Association Specification No. 1 for alloy for dental amalgam. *In* Guide to dental materials, 1962-63. Chicago, 1963.

## Culture Tube and Pipette For Cultivation of Tissues On Standard Microscope Slide

JOSEPH LEIGHTON, M.D.,  
MARTHA ESPER, B.S.



Tissue cultures prepared on coverslips have been used for many years. One of the earliest systems is the double coverslip method of Maximov in which a small coverslip containing adherent tissue fragments is held by the capillary action of a drop of water onto a larger coverslip. The two are inverted with the tissue hanging in the well of a large depression microscope slide. An adap-

---

*Dr. Leighton and Miss Esper are in the department of pathology, School of Medicine, University of Pittsburgh. The study was supported by the Public Health Service through NIH Grant C-2800 and the American Cancer Society through an institutional research grant. The tubes and pipettes described were prepared by the Bellco Co. of Vineland, N.J.*